(54) Negative electrode materials for non-aqueous electrolyte secondary batteries and said batteries employing the same materials

(57) A material of the negative electrode for the non-aqueous electrolyte secondary battery comprises solid phases A and B. A core is formed by the solid phase A of which lithium absorption and desorption amount resulted from charge and discharge is relatively large. The core is partially or entirely wrapped with the solid phase B of which lithium absorption and disorption amount resulted from charge and discharge is not so much as the solid phase A, however, of which discharge capacity decrease a little resulted from cycles. The solid phase A comprises one of the following materials; lithium, at least one of the elements which is able to alloy with lithium, solid solution including at least one of the above elements being able to alloy with lithium, or an intermetallic compound including at least one of the above elements being able to alloy with lithium. The solid phase B has a different composition, but comprises the same kind of materials except lithium by itself as those of the solid phase A. It is essential that the solid phase B is a mixed conductor having electronic conductivity as well as lithium ionic conductivity. When these materials are used in the negative electrode, the non-aqueous electrolyte second battery featuring a high reliability in the safety aspect, high cycle characteristic, a high capacity and excellent high-rate charge and discharge characteristic can be realized.

EP 0 883 199 A1

Description

Background of the Invention

5 **Field of the Invention**

The present invention relates to non-aqueous electrolyte secondary batteries employing organic electrolyte, solid polymer electrolyte or the like, and more particularly to negative electrode materials thereof featuring a high capacity, high reliability for the safety aspect, a little decrease of discharge capacity resulting from cycles, and excellent high-rate
10 charge and discharge characteristics.

Description of the Prior Art

A lithium battery employing lithium as negative active material, in general, generates high electromotive force and
15 can be high energy density. The lithium batteries thus employ various positive active materials combined with the negative active material, and are commercialized to be battery systems, thereby reducing dimensions as well as weights of cordless and portable products.

A lot of effort made both for R&D and commercializing of the lithium batteries is not only for the primary battery, i.e., the battery should be replaced after discharging, but also for the secondary battery, i.e., the battery can be repeatedly
20 used by recharging.

Lithium reacts with water excitedly, and produces hydrogen. Thus, the electrolyte of the lithium batteries employs non-aqueous electrolyte, e.g., 1) organic electrolyte made of dehydrated aprotic organic solvent dissolving lithium salt, and 2) solid polymer electrolyte. The lithium batteries are thus sometimes called non-aqueous electrolyte primary battery and non-aqueous electrolyte secondary battery.

25 As a positive active material of the non-aqueous electrolyte secondary battery, transition metal element oxides including vanadium pentoxide (V_2O_5), titanium disulfide (TiS_2), molybdenum disulfide (MoS_2) and chalcogenide were examined at first; however, recently, lithium contained transition metal element oxides of which transition metal element is partially replaced with another element have been examined. The oxides of lithium contained transition metal element such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ which are double oxides of lithium and cobalt, lithium and nickel, and lithium and
30 manganese. These double oxides repeat desorption and absorption of lithium ion by charge and discharge, whereby excellent cycle life characteristics can be obtained. The chalcogenide, one of the lithium contained transition metal element, is also examined besides these double oxides.

On the other hand, regarding the negative electrode materials, metal lithium which is active material could be the most desirable material from the standpoint of energy density provided it can be used as it is, because an electric poten-
35 tial would be least-noble. However, when this secondary battery is charged, active dendrite or mossy crystal having a large specific surface area deposits on the negative electrode surface, and the crystals thereof react with the solvent in the electrolyte, whereby being deactivated with ease, which lowers the capacity of the battery rapidly, and therefore, a larger quantity of metal lithium must be pre-filled in the negative electrode. Further, the deposited dendrite might penetrate the separator and cause an internal short circuit. These problems shorten the cycle life and affect the product
40 safety.

In order to prevent the dendrite from occurring when the battery is charged, the following materials were tested as a negative electrode material: Li-Al alloy, alloy of Li and Wood's metal which is fusible alloy. When one of these metals which can be alloyed with lithium or such an alloy which contains at least one of these metals is employed as a negative electrode material, the battery indicates a relatively higher capacity at an initial charge and discharge cycle.

45 However, alloying with lithium and lithium elimination are repeated due to charge and discharge, and thus, a phase of the crystal is sometimes changed although a crystal structure of an original skeletal alloy is still maintained, or the crystal structure per se may be changed into a different one from the original skeletal alloy. In such a case, particles of the metal or the alloy, i.e., a host material of lithium which is an active material repeats swelling and shrinking. Along with the progress of charge and discharge cycles, a crystal particle of the metal or the alloy gets cracks, and the parti-
50 cle's fineness progresses finer and finer. Due to this phenomenon, an ohmic resistance between the negative electrode materials increases, and a resistance polarization grows during charge and discharge. As a result, these materials were proved not to satisfy a cycle life characteristic necessary for a practical use.

In recent years, a carbon material such as graphite is employed as a host material of the negative electrode, because such a carbon material is able to absorb and desorb lithium ion by charge and discharge. The carbon material
55 as a negative electrode material, the lithium contained cobalt oxide as a positive electrode material and organic electrolyte are combined to make a system called lithium-ion secondary battery, which is now available in the market.

Further, in order to increase a negative electrode capacity, it is proposed in Japanese Patent Application Laid Open No. H07-315822 that a compound of a host material comprising graphitized carbon material and a material, e.g., silicon

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mixed product incorporated with the host material be employed as a negative electrode material. This laid open application teaches that the battery employing the proposed material has the higher capacity and the longer cycle life than those of the battery which employs silicon alone as a host material of he negative electrode. However, it seems that there is a poor chemical bonding force between silicon and carbon, whereby dimensional swelling of silicon due to absorbing lithium therein cannot be suppressed completely by the carbon around the silicon. As a result, a satisfactory cycle life is not realized.

Other materials are also proposed in the Japanese Patent Application Laid Open Nos. below in order to achieve a high capacity and a long cycle life:

H05-159780: Iron silicide, e.g., Fe_2Si_3, FeSi, $FeSi_2$
H07-240201: transition element and nonferrous metal silicide,
H09-63651: a host material comprising an intermetallic compound including at least one of 4B element, P or Sb and having one of a crystal structure of CaF_2 type, ZnS type or AlLiSi type.

The above materials absorb lithium into crystal lattice thereof by charging, and desorb lithium by discharging. Repeated charge and discharge neither swells nor shrinks the skeletal crystal extensively, and fineness of the crystal particles progresses little. An excellent cycle characteristic thus can be expected.

And yet, the lithium quantity absorbed and desorbed into/from the crystal lattice is limited, those materials thus can not meet the request of the higher capacity, which still remains a problem.

A non-aqueous electrolyte secondary battery as a power supply of an apparatus is required the following features: 1. High capacity, 2. Long cycle life, 3. Chargeable/dischargeable with a high rate. In other words, if a negative electrode material has an extraordinary high capacity but has poor charge and discharge characteristics, it is impossible to reduce both size and weight of the power supply for some applications.

In the non-aqueous electrolyte secondary battery, an electrochemical activity of the particle surface of the negative electrode material is a key factor for improving the charge and discharge characteristics. For instance, in the negative electrode material comprising silicon as a host material, silicon has an advantage such as absorbing and desorbing a lot of lithium during charge-transfer reaction under high-rate charge and discharge. On the other hand, when one of silicides described previously is employed as the negative electrode material, an excellent cycle characteristic can be expected because of superior oxidation and reduction reaction during the charge and discharge according to the function of a mixed conductor for electrons and lithium ions. However, this material has an inferior characteristic of high-rate charge and discharge due to relatively smaller power of absorbing and desorbing lithium.

Summary of the Invention

The present invention aims to provide a negative electrode material for a non-aqueous electrolyte secondary battery, the material features high reliability from the safety view of point, high capacity, less decreasing of discharge capacity due to cycles, and excellent high-rate charge and discharge characteristics.

The present invention covers a composite particle comprises the following elements:

(a) a core formed by solid phase A, and
(b) solid phase B wrapping the core entirely or partially. The solid phase A comprises one of the following elements:

(a-1) lithium,
(a-2) at least one element which is able to alloy with lithium,
(a-3) solid solution including an element which is able to alloy with lithium, or
(a-4) intermetallic compound including an element which is able to alloy with lithium.
The solid phase B has a different composition from the solid phase A, and comprises one of the following elements (b-1) or (b-2):
(b-1) solid solution including (b-3)
(b-2) intermetallic compound including (b-3)
(b-3) at least one element which can alloy with lithium. The composite particle combining the solid phases A and B is employed as the negative electrode material of the non-aqueous electrolyte secondary battery, thereby realizing the battery which meets the requests such as ensuring, a) safety reliability, b) higher capacity, c) less decreasing of discharge capacity due to cycles, and d) excellent high-rate charge and discharge characteristics.

To be more specific, the negative electrode material according to the present invention is realized by the following elements: The composite particle comprises the solid phase A and solid phase B, where the solid phase A is formed

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by at least one of the elements below, or either solid solution or an intermetallic compound, each of them including at least one of the elements below:

zinc, cadmium, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, antimony and bismuth, all of these elements being able to alloy with lithium,
and where the solid phase B is formed by solid solution or intermetallic compound, either one including at least one element selected from alkaline-earth metal elements and transition metal elements.

Brief Description of the Drawings

Fig. 1 is a vertical cross sectional view of a coin type test cell for evaluating charge and discharge efficiency and electrochemical characteristics of negative electrode materials of the present invention.
Fig. 2 is a vertical cross sectional view of a cylindrical cell utilized in an exemplary embodiment of a non-aqueous electrolyte secondary battery having a negative electrode which employs the material of the present invention.

Detailed Description of the Preferred Embodiments

Exemplary embodiments of the present invention are detailed by referring to the attached drawings and tables.

[Embodiment 1]

(1) Preparing powder for the negative electrode material

First, 1) prepare metal lithium and granular element being able to alloy with lithium at a predetermined ratio in an alumina crucible, second, 2) heat the above sample up to an appropriate melting temperature in an electric furnace under dry argon atmosphere, and keep the temperature for one hour, then 3) cool the melted sample down to the room temperature, finally 4) crush the solidified ingot into powder of which each particle size is not more than 150 μm.

(2) Analyzing the section of the prepared powder

First, 1) put the prepared powder into epoxy resin to which curing agent is added, second, 2) knead this sample to disperse the powder, then, 3) de-air substantially and cure the sample, and 4) wrap the sample with epoxy resin, after that, 5) slice the epoxy block in which the prepared powder disperses with a saw in a glove box under dry argon atmosphere, then, 6) polish the section of the sliced block, finally, 7) analyze the polished section with an electronic probe micro analysis (EPMA) method by using JXA-8600MX manufactured by Japan Electronic Co., Ltd.

(3) Measuring an electronic conductivity of the sample powder

Put 3.0g sample powder into a plastic cylinder whose inner diameter is 25 mm. Apply pressure of 408 kgf·cm^{-2} to the sample powder. The plastic cylinder has metallic dies fit into both ends of the cylinder. Insert a metal rod into the cylinder, and measure an ohmic resistance value between the metal dies, (the sample powder is sandwiched between the metal dies,) with LORESTA-SP (MCP-T500) made by Mitsubishi Chemical Co., Ltd., and then find the electronic conductivity from the ohmic resistance.

(4) Measuring an ionic conductivity of the sample powder

Put 3.0g sample powder into a plastic cylinder of which inner diameter is 10 mm, and apply pressure of 2546 kg·cm^{-2} to the powder to mold pellets. The pellet is covered on its both end faces by glassy solid electrolyte, of which thickness is ca. 1.0 mm, and expressed as $0.01 Li_3PO_4 + 0.63 Li_2S + 0.36 SiS_2$. The glossy solid electrolyte has lithium ionic conductivity. Further, cover the outside of the pellet with metal lithium of approx. 1 mm thickness. Then apply pressure of 5093 kgf·cm^{-2} to both faces of the pellet, and measure resistance value with an AC impedance measuring device made by Solartron Co., Ltd. in the U.K. , finally find the lithium ionic conductivity from the measured resistance value.

(5) Evaluating a charge and discharge characteristics of the negative electrode material

Produce a coin type test cell specified as R2016 size (∅ 20.0 mm 1.6 mm overall height) as illustrated in Fig. 1, then measure electrochemical characteristics including charge and discharge capacity, etc. of the negative electrode

material for evaluation.

In Fig. 1, a cell case 1 and a cover 2 both made of stainless steel are sealed gas-tightly and liquid-tightly via a gasket 7 made from polypropylene. A negative material mold electrode 5 is molded with a current collector 3 into one body, meanwhile, the current collector 3 is made of stainless steel expanded metal and welded to an inner bottom face of the cell case 1. A disk-type metal lithium electrode 4 is press fit to an inner face of the cover 2. The negative material mold electrode 5 is separated from the metal lithium electrode 4 by a separator 6 made of microporous polypropylene membrane. Organic electrolyte impregnates between the electrodes and into the negative material mold electrode 5 as well as the separator 6.

The negative material mold electrode 5 is made of predetermined quantity of a mix which is molded with the current collector 3 into one body. The mix comprises (a) negative material powder 85%, (b) binder 10% made of polyvinylidene fluoride and (c) conductive agent 5% made of acetylene black. These percentages represent the relative weight ratios among the materials. After the negative material mold electrode 5 in the cell case 1 is substantially dried under reduced pressure at 80°C, the test cell is assembled.

The organic electrolyte is produced by using the following materials and steps:
Prepare a mixed solvent made from ethylene carbonate (EC) and di-ethyl carbonate (DEC) in an equal volume of each, then, dissolve the solute lithium hexafluorophosphate ($LiPF_6$), which is an electrolyte, into the mixed solvent, and finally, adjust the concentration thereof at $1 \text{ mol} \cdot 1^{-1}$.

The test cell can be interpreted as this: a regular coin-type lithium primary battery, e.g., CR2016 type manganese dioxide lithium battery, of which manganese dioxide positive electrode is replaced with the negative material mold electrode.

The charge and discharge efficiency of the test cell is measured under the following condition: test temperature: 20°C, charge and discharge with current density of $0.5 \text{ mA} \cdot cm^{-2}$ constant current, and discharge up to 3V, then charge down to 0V, repeat this discharge/charge 50 cycles.

Table 1(A) lists the following items; (a) mixing ratios of the raw materials for the negative electrode material prepared, (b) heating temperature, (c) component of the solid phases A and B of the negative electrode material prepared and (d) the electronic conductivity as well as ionic conductivity of the solid phase B.

Table 1(B) lists the following data both at the initial cycle and at the 50th cycle; charge and discharge capacities, efficiency thereof, and the change ratio of discharge capacity, where,

the efficiency of charge and discharge is represented by:

$$(\text{discharge capacity/charge capacity}) \times 100, \text{ and}$$

the change ratio of discharge capacity is represented by

$$(\text{discharge capacity at the 50}^{th} \text{ cycle/discharge capacity at 1}^{st} \text{ cycle}) \times 100.$$

Table 1(B) also lists the following data of the conventional materials in order to show a comparison list with each sample used in the embodiments of the present invention;
For the comparison, produce the negative electrode material based on the same condition as the above sample by using a host material which is able to absorb and desorb lithium ion through charge and discharge, and also produce the test cell based on the same condition, then perform the charge and discharge cycling test. The following conventional materials are employed in this test:

Conventional case 1: silicon powder of which particle size is not more than 150 μm,
Conventional case 2: Put mixed product of silicon powder and naphthalene pitch in the alumina crucible, and then heat it at 1000°C by the electric furnace for one hour under argon atmosphere, then, cool the product down to the room temperature, and crush the product into powder of which particle size is not more than 150 μm. It is confirmed through analysis that the powder is a complex where silicon and carbon are mildly combined.
Conventional case 3: natural graphite powder of which particle size is not more than 150 μm,
Conventional case 4: powder of intermetallic compound Mg_2Si of which particle size is not more than 150 μm,

As Table 1(A) shows, the samples 1-8 used in the exemplary embodiment 1 of the present invention are proved composite particles by EPMA method, i.e., the composite particles comprise the following materials:

(a) solid phase A forming a core comprising metal lithium, and
(b) solid phase B wrapping the solid phase A, the solid phase B comprising an intermetallic compound of lithium and the element being able to alloy with lithium.

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When the above intermetallic compound which forms the solid phase B is independently prepared, and electronic conductivity as well as ionic conductivity of the powder thereof are measured, all the solid phases B are proved as mixed conductors.

The powders of each sample used in the first exemplary embodiment are composite particles formed by peritectic phenomenon.

The discharge capacity at the initial cycle of each sample powder is at least 650 mAh·cm^{-3} which is approximately the same level as those of the conventional case 1 (silicon) and case 2 (complex of silicon and carbon), and higher level than those of the conventional case 3 (natural graphite) and case 4(Mg_2Si).

The efficiencies of charge and discharge at the initial cycle of each sample powder indicate at least 90% that of the conventional case 3 (negative electrode material by natural graphite.)

Regarding the discharge capacity at the 50th cycle, the conventional cases 1 and 2, which indicated large discharge capacities at the initial cycle, show drastic decreases, while the conventional cases 3 (natural graphite) and 4 (Mg_2Si) show little change in the discharge capacities. Each sample powder used in the first exemplary embodiment of the present invention, on the other hand, retains at least 75% of the discharge capacity sustainable rate, and has a larger discharge capacity than those of the conventional cases 3 and 4 by 10-30%.

The metal lithium forming the solid phase A has a high capacity density in itself; however, it shows a drastic decrease in a discharge capacity. The intermetallic compounds of lithium and respective element being able to alloy with lithium, which forms the solid phase B, is the mixed conductor and has excellent cycle characteristics; however, the capacity density thereof is not so high. When the composite particle comprising the solid phases A and B is employed as the negative electrode material, the solid phase B having the excellent cycle characteristics restrains the metal lithium which has high capacity density and forms the solid phase A from being decreased in the discharge capacity due to the charge and discharge cycles, i.e., the solid phases A and B complement each other.

Since the composite particle used in the first exemplary embodiment of the present invention has included lithium (active material) in the form of metal or intermetallic compound, it is appropriate to use this composite particle as the negative electrode material of a battery system such as a practical secondary battery of which operation is started by discharge, while the positive electrode material of this battery system should be selected from oxides and chalcogenides of the transition metal element such as V_2O_5, TiS_2, MoS_2 (these correspond to charged condition), and then, organic electrolyte is impregnated into this material, and finally, the positive electrode is assembled.

[Embodiment 2]

In the second exemplary embodiment, a composite particle comprising the following materials is discussed:

(a) solid phase A which forms a core of the particle, and absorbs and disorbs a large amount of lithium ion by charge and discharge,
(b) solid phase B which wraps the solid phase A, and has excellent cycle characteristics of little decreasing in discharge capacity along the cycle progress, though it has the less absorption and disorption amount of lithium ion than the solid phase A.

(1) Preparing powder of the negative electrode material

Heat two granular element materials, which are able to alloy with lithium at a predetermined ratio, up to an appropriate melting temperature, and then crush the sample into powder same as the first exemplary embodiment.

(2) Analyze the section of the prepared powder, and measuring electronic as well as ionic conductivity

Perform this step according to that of the first exemplary embodiment.

(3) Evaluate the charge and discharge characteristics of the negative electrode material

Form the negative mold electrode same as the first exemplary embodiment, and then produce the test cell under the same condition as the first exemplary embodiment. A different point from the first exemplary embodiment is to start the test by initial charging, while the test in the first exemplary embodiment starts with discharging.

Table 2(A) shows the following data of the solid phases A and B:
mixing ratio, heating temperature of the materials in preparing the negative electrode material, component of the solid phases A and B, and electronic as well as ionic conductivity of the solid phase B.

Table 2(B) shows the following data both at the initial cycle and the 50th cycle of the test cell employing the prepared negative electrode material:

charge and discharge capacities, efficiency of charge and discharge and discharge capacity sustainable rate.
[Note] e.g., in Tables 2(A) and 2(B), the solid phase A of sample No. 15 is indicated as Mn-Al s.s., which means the sample is formed by solid solutions of Mn and Al. The same interpretation can be applied to the sample Nos. 19, 20, 41, 42, 47, 49 and 50, which are formed also solid solutions. The solid phases A of sample Nos. 61, 63 and 65 are formed by single element Mo and Si respectively. The other samples' solid phases A and B are formed by intermetallic compound made from two elements.

Each sample used in the second exemplary embodiment is a composite particle comprising the core formed by the solid phase A, and the solid phase B which wraps the core resulting from peritectic phenomenon. The solid phase B, as shown in Table 2(A), is a mixed conductor having electronic conductivity and lithium ionic conductivity, same as used in the first exemplary embodiment.

Table 2(B) proves that the discharge capacity of each sample in the second exemplary embodiment at the initial cycle is greater than those of the conventional cases 1-4 shown in Table 1(B), in particular, eight samples including the sample Nos. 23, 35, 52, 55, 56, 57, 61 and 63 indicate at least 1000 mAh $\cdot$ cm^{-3} of discharge capacity. These negative electrode materials of high capacity include at least one of the following elements which are able to alloy with lithium (active material) in the solid phase A: zinc, cadmium, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, antimony and bismuth.

The sample No. 65, among others, indicates the largest discharge capacity (1450 mAh $\cdot$ cm^{-3}) of which core comprising the solid phase A is formed by silicon.

Regarding the charge and discharge efficiency at the initial cycle, every sample used in the second exemplary embodiment indicates at least 75% and has a greater charge and discharge efficiency than those of the conventional case 1 (silicon), case 2 (complex of silicon and carbon) and case 4 (Mg$_2$Si); however, many of the samples have less capacity than the conventional case 3 (natural graphite indicated 91%), and yet, several samples (e.g., sample Nos. 9-12, 14, 16, 17 and 19) show not less than the charge and discharge efficiency of the case 3.

Regarding the discharge capacity sustainable rate, every sample indicates at least 75%, and majority of the samples indicate 90% or more. These values are less than the conventional case 3 (natural graphite) and case 4 (Mg$_2$Si). On the other hand, the samples indicate far less decrease of discharge capacity due to cycles than those of the conventional case 1 (silicon) and case 2 (complex of silicon and carbon.)

Based on the data of charge and discharge characteristics both at the initial cycle and 50th cycle, it should be noted that the solid phase A is formed by, as previously described, at least one of the following elements which absorb and desorb a large amount of lithium by charge and discharge:

zinc, cadmium, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, antimony and bismuth,

or formed by either a solid solution or intermetallic compound including an element which is able to alloy with lithium as described above.

The following samples show at least 90% of discharge capacity sustainable rate after the 50th cycle, and thus they are proved to have an excellent cycle characteristic: sample Nos. 2 used in the first exemplary embodiment, sample Nos. 9-17, 19-44, 46-50, 52-61, 63-68 and 70-72 in the second exemplary embodiment.

In the negative electrode materials which show excellent cycle characteristics as described above, it is understandable that the solid phase B is formed by either a solid solution or intermetallic compound including at least one element selected from a group of alkaline earth elements and transition metal elements.

Although Tables 2(A) and 2(B) did not list the following samples, Mg$_2$Si, Mg$_2$Pb, Mg$_2$Sn, Mg$_2$Ge, and transition metal element silicides other than NiSi, such as FeSi$_2$, CoSi$_2$, they have great potentials for forming the solid phase B.

In the sample No. 65 made of composite particles comprising the solid phases A and B, silicon forming the solid phase A is able to alloy with lithium. When silicon alone is employed in the negative electrode as a host material (corresponding to the conventional case 1), an initial charge capacity at the initial cycle indicates, as shown in Table 1(B), 5600 mAh $\cdot$ cm^{-3} as well as such a large amount exceeding 4000 mAh $\cdot$ g^{-1}. However, as the absorption of lithium ion progresses, the crystal structure of silicon changes, i.e., a lattice interval of a crystal expands, and a swelling volume reaches to max. four times, which results in a crack on crystal particle boundaries of silicon.

When silicon is shrunk by the initial discharge, the crystal particles thereof progresses in fineness and becomes finer than those before the initial charge. This progressive fineness increases ohmic contact resistance and lowers electronic conductivity between particles. As a result, over voltage applied to the negative electrode at discharge increases, and thus the discharge capacity at the initial cycle reaches to less than a half of the initial charge capacity. The lithium which has not been utilized as the initial discharge capacity remains in the negative electrode as dead lithium, and does not contribute to charge reaction thereafter.

When the battery is charged at the second cycle, the silicon particle having the higher electric resistance due to progressive fineness finds itself difficult to be alloyed, and only the silicon particle that has a relatively higher electronic conductivity and does not progress in fineness is alloyed, the charge capacity of the battery thus reaches to as low as 20% that of the initial charge. Silicon progresses in fineness at the 2nd cycle discharge, and the discharge capacity further lowers accordingly. Repeating charge and discharge less than 20 cycles brings the battery being unable to charge

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or discharge at all. In the negative electrode in such a condition, the specific surface area increases due to progressive fineness of silicon, and also a lot of dead lithium exists, therefore, the negative electrode is extremely unstable from the thermal view of point, and thus this condition involves safety concern.

The material $NiSi_2$ forming the solid phase B of sample No. 65, on the other hand and different from Si, absorbs and disorbs lithium by charge and discharge within the crystal lattices, thus the crystal structure changes little. As a result, the crystal swells and shrinks little, and the particle fineness does not progress, neither dead lithium nor increasing of the specific surface area can be observed. Accordingly, it is not worth worrying drastic decrease of discharge capacity due to cycles; however, the employment of $NiSi_2$ still cannot provide a satisfactory level of high capacity when a high capacity-oriented battery is desired with the discharge capacity of 250 mAh $\cdot$ g^{-1}. Such a small discharge capacity is disadvantage for evaluating a high rate charge and discharge characteristics.

In the composite particle comprising the solid phases A and B, according to the present invention, a host material of lithium comprising the solid phase A formed by Si and the solid phase B formed by $NiSi_2$ is employed as the negative electrode material. In this case, Si and $NiSi_2$ are bound each other strongly at the boundary face, and easy to be electrically conductive. During the charge and discharge, $NiSi_2$ swells and shrinks far less than Si does, and thus restrains Si from swelling and shrinking within two times of the original volume which is restorable elastic limit for the crystal structure. The amount of lithium absorbed and disorbed by charge and discharge decreases responsive to the restrained amount of Si, and is less than the case where Si alone is used. However, since the solid phase B, which comprises $NiSi_2$, a mixed conductor having electronic and lithium ionic conductivity, wraps the solid phase A comprising Si, electrons can move between Si and $NiSi_2$ as described above. When lithium ion is absorbed into Si as well as $NiSi_2$ from non-aqueous electrolyte by charging, electrons are provided from electron cloud which is formed by mixing Si and NiSi2. Therefore, the total lithium amount absorbed into Si and $NiSi_2$ is less than the case of Si alone, and yet, it is substantially greater than the case of $NiSi_2$ alone.

The above description proves that when the composite particle formed by the solid phases A (Si) and B ($NiSi_2$) according to the present invention is employed as the negative electrode material, the negative electrode shows the less decrease of discharge capacity due to cycles, and has the greater capacity than those of the conventional case 3 (natural graphite) and case 4 (Mg_2Si) both of which have excellent cycle characteristics and relatively high capacities.

The safety of the negative electrode material for non-aqueous electrolyte secondary battery is tested with "solder iron method" named by the inventors' group. The method is as follows: First, charge the test cell which underwent the 50-cycle charge and discharge test, and second, disassemble the test cell in a glove box under dry air of less than 5% relative humidity, then, dry vacuum the disassembled cell. Then, press a solder iron heated up to ca. 300°C to the negative material mold electrode 5 which has been molded with the current collector 3 into one body still remained in the cell case. Then, the following phenomena are observed:

Conventional case 1 (Si); The sample generates white fuming, but no spark or combustion.
Conventional case 2 (complex of Si and Co) and case 3 (natural graphite); The sample is burnt excitedly.
Conventional case 4 ($MgNi_2$); No change in appearance is observed.

Embodiment 1 and Embodiment 2 of the present invention; There are no white fuming, spark, or combustion, thus no change is observed. As a result, the samples of the present invention are proved to be the most reliable from the safety view of point.

It can be concluded that the negative electrode material comprising the composite particles formed by the solid phases A and B is highly safety and has the less decrease of discharge capacity due to cycles as well as the higher capacity than the conventional materials.

[Embodiment 3]

In the third exemplary embodiment, variation of a material mixing ratio (at.%) between Si and Ni, particle size (average) variation due to pulverize, and resulting specific surface area variation thereof, are discussed what influences these variations give the charge and discharge characteristics.

(1) Preparing powder of the negative electrode material.
Vary the raw material mixing ratio between granular Ni and Si, and heat each sample up to an appropriate melting temperature, then crush an ingot same as the first exemplary embodiment, then sift the sample into several groups based on an average particle size.
(2) Measuring the average particle size.
Measure the average particle size with the particle size distribution measuring method by LASER.
(3) Measuring the specific surface area of the prepared powder using BET method by N_2 gas adorption.
(4) Measuring a percentage content of nickel silicide in the prepared powder.

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Dissolve the prepared powder into hydrochloric acid, and drop ethanol solution of dimethylglyoxime so that dimethylglyoximat-nickel (II) deposits, then, find the total amount of nickel, finally, convert the amount into NiSi2 as the percentage content of nickel silicide.

(5) Evaluating the charge and discharge characteristics of the negative electrode materials.

Form a negative material mold electrode same as the first exemplary embodiment, and then, produce a test cell under the same condition as the first exemplary embodiment. Repeat charge and discharge 50 cycles on the test cell under the same condition as the second exemplary embodiment.

The test result is shown in Table 3. In order to compare each sample in the third exemplary embodiment with the conventional materials, Table 4 lists the following data: Each sample of the conventional cases 1-4 are sifted into several groups depending on the particle size, each group thus has a specific surface area responsive to the particle size. Each group undergoes 50 cycles of charge and discharge. The test result is listed in Table 4.

As Tables 3 and 4 indicate, Sample Nos. 74 a-f (the percentage content of the solid phase B is 30%, and the solid phase B is assumed $NiSi_2$) drastically lower the discharge capacity sustainable rate down to as low as 20-30% after the 50th cycle. On the other hand, Sample Nos. 75 a-f, 76 a-f, 77 a-f and 78 a-f maintain the rate at as high as 97-98%. In the case of Sample Nos. 74 a-f, the percentage content of $NiSi_2$ which forms the solid phase B is rather low at 30%, and the percentage content of Si in the solid phase A is high. This composition drastically lowers the discharge capacity along with the progressive cycles although a high capacity of charge and discharge is reserved at the initial cycle. This data proves that the presence of $NiSi_2$ in the solid phase B at a low percentage content cannot restrain Si from swelling and shrinking due to charge and discharge.

Sample Nos. 78 a-f which have the higher percentage content of $NiSi_2$ in the solid phase B, on the other hand, retain the discharge capacity sustainable rate due to cycles at as high as 98%, however, the charge and discharge capacities thereof are not larger than those of Sample No. 65 in the second exemplary embodiment, Sample Nos. 75 a-f, 76 a-f and 77 a-f in this exemplary embodiment. An excessively low percentage content of Si forming the solid phase A causes this phenomenon.

The nickel silicide forming the solid phase B is assumed $NiSi_2$ in this embodiment; however, there are many nickel silicide such as $NiSi$, Ni_3Si_2, Ni_2Si, etc. However, it is practically impossible to separate these materials quantatively, thus, a main component $NiSi_2$ is described representatively.

It is concluded that the appropriate percentage content of nickel silicide (assuming $NiSi_2$) forming the solid phase B ranges between 40-95 weight %.

Regarding the percentage content in the solid phase B, the case where the solid phase A formed by Si and the solid phase B formed by $NiSi_2$ has been detailed. In the case of the first exemplary embodiment and the second exemplary embodiment, each sample shows an excellent charge and discharge characteristics when the percentage content thereof in the solid phase B ranges the same limits, i.e., 40-95%.

When the average particle size becomes smaller, the responsive specific surface area thereof increases. This phenomenon is observed in each sample used in this third exemplary embodiment and the conventional cases 1-4.

Regarding each samples in this third exemplary embodiment, a correlation between the average particle size and the charge and discharge capacities both at the initial and 50th cycles is verified; A distinct difference is observed between two groups having different ranges of average particle size, i.e., 100-50 μm and 40-0.5 μm. In the case of the first group having 100-50 μm average particle size has lower charge and discharge capacity than the second group having 40-0.5 μm by ca. 200 mAh • cm^{-3}. When the particles have a larger average size such as 100-50 μm, diffusion in the solid phase delays, and thus an over voltage increases, which lowers the charge and discharge capacity.

As indicated in Table 4, the conventional samples 1 a-f through 4 a-f show the following phenomena:

Conventional sample 3 a-f: Natural graphite is proved an excellent material for the negative electrode because of a) extremely high efficiency of charge and discharge both at the initial and 50th cycles, and b) extremely small decrease in discharge capacity due to cycles, however, the charge and discharge capacities thereof does not reach to 500 mAh• cm^{-3}, therefore, natural graphite is not appropriate for high capacity oriented battery. These characteristics are not changed by variation of the average particle size.

Conventional samples 1 a-f and 2 a-f: The complex of silicon and carbon shows a poor cycle characteristic, and this is not improved by the variation of average particle size.

Conventional samples 4 a-f: Mg_2Si shows low efficiency of charge and discharge at the initial cycle. As same as the conventional samples 3 a-f, Mg_2Si shows little decrease in the discharge capacity due to cycles, and yet the charge and discharge capacity at the 50th cycle does not reach to 500 mAh cm^{-3}, accordingly, Mg_2Si is not appropriate for the high-capacity oriented battery. These characteristics are not changed by the variation of average particle size.

Based on the above discussion, it is proved that the samples of each exemplary embodiment according to the present invention have the better charge and discharge characteristics than those of the conventional samples.

The test cells undergone the 50 cycles of charge and discharge test is charged again for evaluating the safety of each negative electrode material by the "solder iron method." Here is the evaluation report:

Sample Nos. 74 a-f: White fuming is observed in every sample, for due to low percentage content of NiSi$_2$ forming the solid phase B, the presence of NiSi$_2$ cannot restrain Si forming the solid phase A from swelling and shrinking, and thus these samples react in the same way as the negative electrode material which employs Si alone did.

Sample Nos. 75 a-f through 78 a-f: A little white fuming is observed in Sample Nos. 75a, 76a, 77a and 78a of which average particle size is 0.5 μm.

In this case, a specific surface area is larger than 10 m^{2}g^{-1}, which means an active surface area has majority, thus concerns are involved in the safety aspect.

Other samples do not show any white fuming, spar, or combustion, and they have no problem in the safety as Sample No. 65 did in the second exemplary embodiment.

As a result, an excellent negative electrode material can be specified as follows based on the third exemplary embodiment:

the solid phase A is formed by Si,
the solid phase B is formed by NiSi2,
the average particle size ranges between 1 and 40 μm,
the specific surface area ranges between 0.01 and 10 m^{2}g^{-1}

The material having the above specifications has an excellent charge and discharge characteristics and has no problem in safety. The above specification, however, has a premise that the percentage content of nickel silicide forming the solid phase B ranges between 40 weight % and 95 weight %, as previously described.

[Embodiment 4]

When every sample used in each exemplary embodiment is observed in its section through electron microscope, the core comprising the solid phase A reveals that it is not always wrapped up completely with the solid phase B. In the fourth exemplary embodiment, an exposed area of Si on a particle which forms the solid phase A vs. total surface area of the particle is discussed what influence this factor gives the charge and discharge characteristics. Samples used in this fourth exemplary embodiment are the same composite particle as those used in the third exemplary embodiment, and Sample No. 65 in the second exemplary embodiment, i.e., the solid phase A is formed by Si, and the solid phase B is formed by nickel silicide.

(1) Preparing powder of the negative electrode material

Vary the raw material mixing rate of granular Si and Ni, and heat the samples up to a responsive appropriate melting temperature. After the powder of the sample is obtained, the powder is sorted into the following several groups through EPMA and an electron microscope: Silicon exposed area ratio against the overall particle surface area are 0, 2, 5, 10, 20, 40, 60, and 100%. In the case of 100% ratio, the negative electrode material made from Si alone which is used in the conventional case 1 is employed.

(2) Evaluating the charge and discharge characteristics of the samples

Form a negative material mold electrode same as the first exemplary embodiment, and produce a test cell under the same condition as the first exemplary embodiment. Charge the test cell with 0.5 mA·cm^{-2} at 20°C, then, discharge it down to 3.0V with varying the discharge rate such as 0.5, 0.7, 1.4, 2.0 and 3.0 mA·cm^{-2}. The discharge capacity at the lowest discharge rate 0.5 mA·cm^{-2} is expressed 100, and find the discharge capacity ratio at each discharge rate. The indications found are called "change ratio of discharge capacity." These information is listed in Table 5.

When the Si exposed area ratio is 5% or more against the overall surface area of the particle of negative electrode material, the material is proved to have an excellent high rate discharge characteristic. However, when the Si expose ratio reaches to as high as 40% or more, the amount of Si forming the solid phase A is excessive, which lowers the cycle characteristic. Accordingly the Si exposed area ratio is preferably adjusted to range between 5% and 40%. This condition is effective both at high rate charge and high rate discharge.

When the overall surface area of the particle is wrapped up completely with nickel silicide forming the solid phase B, the sample does not always show an excellent high rate charge and discharge characteristics, as described above. When Si of the solid phase A is exposed on the particle surface at an appropriate exposing ratio, this exposed Si can absorb and desorb a lot of lithium, and thus a speed of a lithium absorption and desorption is accelerated by this Si together with the nickel silicide. As a result, the high rate charge and discharge characteristics are improved.

[Embodiment 5]

Use Sample No. 65 in the second exemplary embodiment as the negative electrode material, and select one of the following materials as a positive electrode material, then produce a cylindrical cell having a nominal capacity 780 mAh (overall height: 50 mm, outer diameter: 17 mm) as shown in Fig. 2. The cylindrical cell undergoes the charge and discharge cycle test.

Materials for the positive electrode: lithium contained cobalt oxides ($LiCoO_2$), lithium contained nickel oxides, spinel-type lithium contained manganese oxides ($LiMn_2O_4$).

The cylindrical cell shown in Fig. 2 is assembled through the following steps:

(a) Roll an electrode group comprising a positive electrode plate 8, a negative electrode plate 10 and a microporous polyporpylene membrane 12 as the separator inserted between the plates 8 and 10.

(b) Mount an upper insulating plate 13 and a lower insulating plate 14 made of polypropylene to the rolled electrode group.

(c) Put the above assembled electrode group and insulating plates into a cell case 15 made of nickel plated steel.

(d) Weld one end of a positive lead tab 9 to a lower surface of a cover 16 into which an explosion-proof mechanism has been built. The cover 16 is coupled with a gasket 17 made of polypropylene.

(e) Weld one end of a negative lead tab 11 which has been welded to the negative electrode 10 to an inside bottom surface of the cell case 15.

(f) Pour predetermined amount of organic electrolyte as non-aqueous electrolyte.

(g) After the electrolyte is absorbed and impregnated into the electrode group, seal an upper edge of the cell case 15 and the cover 16 through the gasket 17 liquid-tightly as well as gas-tightly.

(h) Provide the sealed cell case with an insulating package (not shown) to complete the cell.

The positive electrode 8 is produced through the following steps:

Prepare the following materials: three kinds of powders of positive electrode material (100 weight), carbon black as conductive agent (2.5 weight), aquatic-dispersion solution of polytetrafluoroethylene as binder (7 weight).

Knead the above prepared materials into paste,

coat both sides of aluminum foil (core material) with the paste,

dry the paste, and then, roll the coated foil with pressure,

cut the rolled foil into a plate having a predetermined size, and mount the positive lead tab 9 made of titan to the plate by spot welding.

The negative electrode 10 is produced through the following steps:

Prepare Sample No. 65, which comprises the solid phase A formed by Si and the solid phase B formed by $NiSi_2$, as a negative electrode material,

add polyvinylidene fluoride (PVDF) as binder and natural graphite,

knead the above mixed materials into paste,

coat both sides of copper foil (core material) with the paste,

dry the paste, roll the foil with pressure,

cut the rolled foil into a plate having a predetermined size, and mount the negative lead tab 11 made of copper to the plate by spot welding.

The organic electrolyte used in the coin type test cell is employed as non-aqueous electrolyte, i.e., dissolve LiPF6 into the mixed solvent comprising the same volume of EC (ethylene carbonate) and DEC (di-ethyl carbonate).

Table 6 shows the following data: Vary the component of the negative electrode paste responsive to each positive electrode material, then measure the discharge capacities of every combination at the initial cycle and after the 500th cycle, and calculate the discharge capacity sustainable rate.

The condition of charge and discharge test is as follows:

repeat charge and discharge with a constant current of 0.2 CmA (156 mA) at 20°C,

charge end voltage: 4.2V

discharge end voltage: 3.0V

As shown in Table 6, when the percentage content of natural graphite powder in the negative electrode paste ranges between 5-80 weight %, the discharge capacity sustainable rate after the 500th cycle stays at least 80%, rela-

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tively higher value for each positive electrode material. On the other hand, when the percentage content is less than 5 weight %, the electronic conductivity lowers and the over voltage increases, thus, the cycle characteristic lowers. However, when the percentage content exceeds 80 weight %, the cycle characteristic also lowers because the diffusion resistance of lithium ion increases, thereby increasing non-reacted part within the plate. Therefore, it is desirable to adjust the percentage content of natural graphite powder between 5-80 weight %.

In this embodiment, the natural graphite powder is detailed, however, other materials such as carbon black including acetylene black, and carbon materials including artificial graphite, graphitisable carbon such as mesophase micro beads, fibrous graphite, and nongraphitisable carbon can be also employed.

In this embodiment, the mixed solution comprising the same volume of EC and DEC is described as the organic electrolyte, however, the following materials can be used as an electrolyte: lithium salts such as lithium perchlorate ($LiCl_4$), lithium tetrafluoroborate ($LiBF_4$), lithium trifluoromethane sulfonate ($LiCF_3SO_3$), lithium hexafluoroarsenate ($LiAsF_6$), and organic solutions including circular ester such as propylene carbonate, circular ether such as tetrahydrofuran, chain ether such as di-methoxyethan, chain ester such as methylpropionate, as itself alone, and mixed solvent two kinds or more.

Further, it is not necessary to limit the electrolyte to the organic electrolyte, and thus solid polymer electrolyte, gel polymer electrolyte having organic solvent as plasticizer in addition to the solid polymer electrolyte can be used.

The test cell used in every embodiment is coin type and cylindrical, however, effect of the present invention does not change depending on a cell shape. The same effect can be expected in a square type cell as well as a sheet type thin-cell.

The positive electrode materials are not necessarily limited to three materials shown in the fifth exemplary embodiment. As described in the first exemplary embodiment, V_2O_5, TiS_2, MoS_2, etc. can be employed.

In each exemplary embodiment, all the samples of the negative electrode materials are described to comprise two types of elements such as lithium and an element being able to alloy with lithium; however, the material can be prepared by using more than three elements upon request.

Table 1(A)

	Raw Materials Mixing Ratio (at.%)		Heating temperature (°C)	Component of negative electrode materials		Conductivity of solid phase B (S·cm⁻¹)	
	I	II		Solid phase A	Solid phase B	Electronic conductivity	Ion conductivity
Sample No. 1	Li:67	Al:33	600	Li	Li_2Al	10^0 order	10^{-5} order
Sample No. 2	Li:75	Cd:25	400	Li	Li_3Cd	10^0 order	10^{-5} order
Sample No. 3	Li:80	Bi:20	1200	Li	Li_3Bi	10^0 order	10^{-5} order
Sample No. 4	Li:82	Sn:18	800	Li	Li_4Sn	10^0 order	10^{-5} order
Sample No. 5	Li:50	Zn:50	500	Li	$LiZn$	10^0 order	10^{-5} order
Sample No. 6	Li:80	Tl:20	400	Li	Li_4Tl	10^0 order	10^{-5} order
Sample No. 7	Li:80	Pb:20	750	Li	Li_4Pb	10^0 order	10^{-5} order
Sample No. 8	Li:60	In:40	500	Li	$LiIn$	10^0 order	10^{-5} order

Table 1(B)

	Component of negative electrode material		Initial cycle			50th cycle			Discharge Capacity Sustainable rate(%)
	Solid Phase (A)	Solid phase (B)	Charge capacity (mAh.cm⁻³)	Discharge capacity (mAh.cm⁻³)	Efficiency of charge & discharge (%)	Charge capacity (mAh.cm⁻³)	Discharge capacity (mAh.cm⁻³)	Efficiency of charge & discharge 0	
Sample No. 1	Li	Li_2Al	699	650	93	645	501	78	77
Sample No. 2	Li	Li_3Cd	773	665	92	631	606	96	91
Sample No. 3	Li	Li_3Bi	736	670	91	650	514	76	77
Sample No. 4	Li	Li_4Sn	740	688	93	678	529	78	77
Sample No. 5	Li	$LiZn$	712	655	92	634	602	95	92
Sample No. 6	Li	Li_4Tl	717	667	93	639	505	79	76
Sample No. 7	Li	Li_4Pb	794	715	90	700	560	80	78
Sample No. 8	Li	$LiIn$	775	705	91	691	560	81	79
Conventional case 1	Si		5600	840	15	10	1	10	0
Conventional case 2	Si+C		2300	599	26	105	16	15	3
Conventional case 3	C(Natural Graphite)		490	448	91	446	445	100	99
Conventional case 4	Mg_2Si		1120	461	41	451	449	100	97

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Table 2(A)

	Raw Materials mixing Ratio (at.%)		Heating temperature (°C)	Component of negative materials	electrode	Conductivity of solid phase B (S·cm⁻¹)	
	I	II		Solid phase A	Solid phase B	Electronic conductivity	Ion conductivity
Sample No. 9	Al:67	Ba:33	1100	$BaAl_4$	$BaAl_2$	10^0 order	10^{-4} order
Sample No. 10	Al:80	Ca:20	970	$CaAl_2$	$CaAl_4$	10^0 order	10^{-4} order
Sample No. 11	Al:80	Ce:20	1300	$CeAl_2$	$CeAl_2$	10^0 order	10^{-5} order
Sample No. 12	Al:82	Co:18	1150	Co_2Al_5	Co_2Al_9	10^0 order	10^{-4} order
Sample No. 13	Al:80	Cr:20	1150	$CrAl_3$	$CrAl_4$	10^0 order	10^{-4} order
Sample No. 14	Al:75	Fe:25	1200	Fe_2Al_5	$FeAl_3$	10^0 order	10^{-4} order
Sample No. 15	Al:77	Mn:23	1140	Mn-Al s.s.	$MnAl_3$	10^0 order	10^{-4} order
Sample No. 16	Al:75	Ni:25	1120	Ni_2Al_3	$NiAl_3$	10^0 order	10^{-4} order
Sample No. 17	Al:75	Pd:25	920	Pd_2Al_3	$PdAl_3$	10^0 order	10^{-4} order
Sample No. 18	Al:84	Te:16	810	Al_2Te_3	Al_5Te	10^0 order	10^{-5} order
Sample No. 19	Al:75	Th:25	1450	Al-Th s.s.	$ThAl_3$	10^0 order	10^{-4} order
Sample No. 20	Al:75	Ti:25	1380	Ti-Al s.s.	$TiAl_3$	10^0 order	10^{-3} order
Sample No. 21	Al:75	V:25	1430	V_5Al_5	VAl_3	10^0 order	10^{-3} order
Sample No. 22	Al:93	W:7	1280	WAl_5	WAl_{12}	10^0 order	10^{-4} order
Sample No. 23	Ba:20	Mg:80	680	Mg_9Ba	Mg_4Ba	10^0 order	10^{-4} order
Sample No. 24	Ba:50	Pb:50	900	Ba_2Pb	$BaPb$	10^0 order	10^{-3} order
Sample No. 25	Ba:83	Sn:17	700	$BaSn_3$	$BaSn_5$	10^0 order	10^{-4} order
Sample No. 26	Bi:75	Ca:25	680	$BaCa_3$	Bi_3Ca	10^0 order	10^{-4} order
Sample No. 27	Bi:67	Ce:33	1350	·BiCe	Bi_2Ce	10^0 order	10^{-4} order
Sample No. 28	Bi:75	Ni:25	780	$NiBi$	$NiBi_3$	10^0 order	10^{-4} order
Sample No. 29	Bi:67	Rh:33	850	$RhBi$	$RhBi_2$	10^0 order	10^{-5} order
Sample No. 30	Ca:67	Si:33	1000	$CaSi$	Ca_2Si	10^0 order	10^{-3} order
Sample No. 31	Ca:33	Si:67	1190	$CaSi$	$CaSi_2$	10^0 order	10^{-4} order
Sample No. 32	Ca25	Tl:75	570	Ca_3Tl_4	$CaTl_3$	10^0 order	10^{-5} order
Sample No. 33	Ca:50	Zn:50	670	$CaZn_2$	$CaZn$	10^0 order	10^{-4} order
Sample No. 34	Cu:25	Cd:75	570	Cu_5Cd_8	$CuCd_3$	10^0 order	10^{-5} order
Sample No. 35	Mg:67	Ce:33	820	Mg_3Ce	Mg_2Ce	10^0 order	10^{-3} order
Sample No. 36	Zn:8	Ce:92	1000	$CeZn_8$	$CeZn_{11}$	10^0 order	10^{-5} order
Sample No. 37	Co:40	Ge:60	980	CoG_5	Co_2Ge_3	10^0 order	10^{-5} order
Sample No. 38	Co:33	Sb:67	1100	$CoSb$	$CoSb_2$	10^0 order	10^{-3} order
Sample No. 39	Co:33	Sn:67	1100	$CoSn$	$CoSn_2$	10^0 order	10^{-3} order
Sample No. 40	Cr:33	Sb:67	1000	$CrSb$	$CrSb_2$	10^0 order	10^{-4} order
Sample No. 41	Cu:68	Sb:32	670	Sb-Cu s.s.	Cu_2Sb	10^0 order	10^{-5} order
Sample No. 42	Fe:33	Sb:67	950	Fe-Sb s.s.	$FeSb_2$	10^0 order	10^{-5} order
Sample No. 43	Ni:20	Ga:80	900	Ni_2Ga_3	$NiGa_4$	10^0 order	10^{-5} order
Sample No. 44	Pr:50	Ga:50	1250	$PrGa_2$	$PrGa$	10^0 order	10^{-6} order

Table 2(A) [continued]

	Raw Materials mixing Ratio (at.%)		Heating temperature (°C)	Component of negative electrode materials		Conductivity of solid phase B (S·cm⁻¹)	
	I	II		Solid phase A	Solid phase B	Electronic conductivity	Ion conductivity
Sample No. 45	Ga:25	Te:75	650	Ga_2Te_3	$GaTe_3$	10^0 order	10^{-5} order
Sample No. 46	Mn:60	Ge:40	980	Mn_5Ge_3	Mn_3Ge_2	10^0 order	10^{-6} order
Sample No. 47	Ni:50	Ge:50	950	Ni-Gess	NiGe	10^0 order	10^{-4} order
Sample No. 48	Zr:75	Ge:25	2200	Zr_2Ge	Zr_3Ge	10^0 order	10^{-5} order
Sample No. 49	Mn:75	In:25	1000	Mn-Ins.s.	Mn_3In	10^0 order	10^{-5} order
Sample No. 50	Ni:50	In:50	970	Ni-Ins.s.	NiIn	10^0 order	10^{-4} order
Sample No. 51	In:28	Te:72	650	In_2Te_3	In_2Te_5	10^0 order	10^{-5} order
Sample No. 52	Mg:90	La:10	760	Mg_3La	Mg_9La	10^0 order	10^{-5} order
Sample No. 53	La:33	Sb:67	1350	LaSb	$LaSb_2$	10^0 order	10^{-4} order
Sample No. 54	La:8	Zn:92	1000	$LaZn_3$	$LaZn_{13}$	10^0 order	10^{-5} order
Sample No. 55	Mg:67	Ni:33	900	$MgNi_2$	Mg_2Ni	10^0 order	10^{-5} order
Sample No. 56	Mg:90	Pr:10	720	Mg_3Pr	Mg_9Pr	10^0 order	10^{-5} order
Sample No. 57	Mg:75	Sr:25	700	Mg_2Sr	$Mg_{23}Sr$	10^0 order	10^{-5} order
Sample No. 58	Mg:50	Zn:50	570	$MgZn_2$	MgZn	10^0 order	10^{-3} order
Sample No. 59	Mn:77	Si:23	1160	Mn_5Si_3	Mn_3Si	10^0 order	10^{-5} order
Sample No. 60	Mn:33	Sn:67	730	Mn_2Sn	$MnSn_2$	10^0 order	10^{-4} order
Sample No. 61	Mo:50	Ni:50	1750	Mo	MoNi	10^0 order	10^{-5} order
Sample No. 62	Mo:75	Si:25	2200	Mo_3Si_2	Mo_3Si	10^0 order	10^{-4} order
Sample No. 63	Mo:67	Zr:33	2150	Mo	$ZrMo_2$	10^0 order	10^{-5} order
Sample No. 64	Ni:32	Sb:68	1060	NiSb	$NiSb_2$	10^0 order	10^{-5} order
Sample No. 65	Ni:20.4	Si:79.6	1250	Si	$NiSi_2$	10^0 order	10^{-6} order
Sample No. 66	Ni:43	Sn:57	1160	Ni_3Sn_2	Ni_3Sn_4	10^0 order	10^{-5} order
Sample No. 67	Pd:50	Pb:50	680	Pd_3Pb_2	PdPb	10^0 order	10^{-6} order
Sample No. 68	Pr:67	Tl:33	1100	PrTl	Pr_2Tl	10^0 order	10^{-5} order
Sample No. 69	Tl:40	Se:60	330	TlSe	Tl_2Se_3	10^0 order	10^{-5} order
Sample No. 70	Zr:33	Si:67	570	ZrSi	$ZrSi_2$	10^0 order	10^{-5} order
Sample No. 71	Sn:83	Sn:17	580	$SrSn_3$	$SrSn_5$	10^0 order	10^{-5} order
Sample No. 72	Zr:33	Sn:67	1570	Zr_3Sn_2	$ZrSn_2$	10^0 order	10^{-5} order
Sample No. 73	Tl:50	Te:50	370	Tl_3Te_2	TlTe	10^0 order	10^{-5} order

Table 2(B)

	Composition of negative electrode materials		Initial cycle			50th cycle			Discharge capacity sustainable rate(%)
	Solid Phase (A)	Solid phase (B)	Charge capacity (mAh.cm^{-3})	Discharge capacity (mAh.cm^{-3})	Efficiency of charge & discharge (%)	Charge capacity (mAh.cm^{-3})	Discharge capacity (mAh.cm^{-3})	Efficiency of charge & discharge (%)	
Sample No. 9	$BaAl_4$	$BaAl_2$	1200	1100	92	1050	1000	95	91
Sample No 10	$CaAl_2$	$CaAl_4$	1180	1090	92	1043	998	96	92
Sample No.11	$CeAl_2$	$CeAl_4$	1225	1115	91	1085	1042	96	93
Sample No.12	Co_2Al_5	Co_2Al_9	1237	1126	91	1103	1059	96	94
Sample No.13	$CrAl_4$	$CrAl_7$	1234	1098	89	1040	998	96	91
Sample No.14	Fe_2Al_5	$FeAl_3$	1111	1020	92	992	945	95	93
Sample No.15	Mn-Al s.s.	$MnAl_3$	1120	1010	90	1001	950	95	94
Sample No.16	Ni_2Al_3	$NiAl_3$	1170	1088	93	1045	1003	96	92
Sample No 17	Pd_2Al_3	$PdAl_3$	1163	1070	92	1027	996	97	93
Sample No 18	Al_2Te_3	Al_5Te	1322	1150	87	1092	863	79	75
Sample No 19	Al-Th s.s.	$ThAl_3$	1341	1220	91	1186	1150	97	94
Sample No 20	Ti-Al s.s.	$TiAl_3$	1271	1100	87	1045	1001	96	91
Sample No 21	V_5Al_5	VAl_3	1310	1170	89	1099	1063	97	91
Sample No 22	WAl_5	WAl_{12}	1421	1250	88	1228	1167	95	93
Sample No 23	Mg_9Ba	Mg_4Ba	945	810	86	802	765	95	94
Sample No 24	Ba_2Pb	$BaPb$	1178	1060	90	1042	990	95	93
Sample No 25	$BaSn_3$	$BaSn_5$	1422	1280	90	1258	1195	95	93
Sample No 26	$BiCa_3$	Bi_3Ca	1299	1143	88	1123	1067	95	93
Sample No 27	$BiCe$	Bi_2Ce	1582	1250	79	1210	1163	96	93
Sample No 28	$NiBi$	$NiBi_3$	1420	1150	81	1138	1081	95	94
Sample No 29	$RbBi$	$RbBi_2$	1465	1143	78	1107	1052	95	92
Sample No 30	$CaSi$	Ca_2Si	1150	1020	89	956	918	96	90
Sample No 31	$CaSi$	$CaSi_2$	1210	1065	88	1020	970	95	91
Sample No 32	Ca_3Tl_4	$CaTl_3$	1326	1180	89	1145	1099	96	93
Sample No 33	$CaZn_2$	$CaZn$	1310	1100	84	1108	150	95	95
Sample No 34	Cu_5Cd_8	$CuCd_3$	1375	1210	88	1148	1113	97	92
Sample No 35	Mg_3Ce	Mg_2Ce	709	610	86	577	554	96	91
Sample No 36	$CeZn_9$	$CeZn_{11}$	1469	1190	81	1165	1107	95	93
Sample No 37	CoG_6	Co_2Ge_3	1428	1157	81	1127	1082	96	94
Sample No 38	$CoSb$	$CoSb_2$	1511	1250	83	1173	1138	97	91
Sample No 39	$CoSn$	$CoSn_2$	1463	1212	83	1175	1139	97	94
Sample No 40	$CrSb$	$CrSb_2$	1320	1050	80	1039	998	96	95
Sample No 41	Sb-Cu s.s.	Cu_2Sb	1290	1070	83	1014	974	96	91
Sample No 42	Fe-Sb s.s.	$FeSb_2$	1390	1209	87	1184	1137	96	94
Sample No 43	Ni_2Ga_3	$NiGa_4$	1458	1123	77	1111	1056	95	94
Sample No 44	$PrGa_2$	$PrGa$	1748	1311	75	1312	1246	95	95

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Table 2(B) [continued]

	Composition of negative electrode materials		Initial cycle			50th cycle			Discharge capacity sustainable rate(%)
	Solid Phase (A)	Solid phase (B)	Charge capacity (mAh.cm^{-3})	Discharge capacity (mAh.cm^{-3})	Efficiency of charge & discharge (%)	Charge capacity (mAh.cm^{-3})	Discharge capacity (mAh.cm^{-3})	Efficiency of charge & discharge (%)	
Sample No.45	Ga$_2$Te$_3$	GaTe$_3$	1660	1295	78	1184	971	82	75
Sample No 46	Mn$_5$Ge$_3$	Mn$_3$Ge$_2$	1987	1351	68	1324	1271	96	94
Sample No.47	Ni-Gess	NiGe	1686	1366	81	1341	1301	97	95
Sample No.48	Zr$_2$Ge	Zr$_3$Ge	1701	1157	68	1133	1088	96	94
Sample No.49	Mn-Inss	Mn$_3$In	1397	1201	86	1159	1113	96	93
Sample No.50	Ni-Inss	NiIn	1296	1089	84	1075	1021	95	94
Sample No.51	In$_2$Te$_3$	In$_2$Te$_5$	1609	1223	76	1168	911	78	75
Sample No.52	Mg$_3$La	MgLa	923	714	77	684	650	95	91
Sample No 53	LaSb	LaSb$_2$	1360	1156	85	1144	1098	96	95
Sample No 54	LaZn$_8$	LaZn$_{13}$	1172	1055	90	1044	992	95	94
Sample No 55	MgNi$_2$	Mg$_2$Ni	726	610	84	578	561	97	92
Sample No 56	Mg$_3$Pr	Mg$_9$Pr	912	786	86	753	715	95	91
Sample No 57	Mg$_2$Sr	Mg$_3$Sr	827	727	88	689	662	96	91
Sample No 58	MgZn$_2$	MgZn	1323	1115	84	1099	1055	96	95
Sample No 59	Mn$_5$Si$_3$	Mn$_3$Si	1451	1277	88	1250	1213	97	95
Sample No 60	Mn$_2$Sn	MnSn$_2$	1211	1050	87	1039	987	95	94
Sample No 61	Mo	MoNi	763	641	84	608	583	96	91
Sample No 62	Mo$_3$Si$_2$	Mo$_3$Si	1425	1233	87	1211	981	81	80
Sample No 63	Mo	ZrMo$_2$	94	699	88	681	667	98	95
Sample No 64	NiSb	NiSb$_2$	1488	1255	84	1246	1196	96	95
Sample No 65	Si	NiSi$_2$	1611	1450	90	1496	1421	95	98
Sample No 66	Ni$_3$Sn$_2$	Ni$_3$Sn$_4$	1588	1399	88	1355	1301	89	93
Sample No 67	Pd$_3$Pb$_2$	PdPb	1509	1298	86	1223	1186	97	91
Sample No 68	PrTl	Pr$_2$Tl	1579	1405	89	1345	1278	95	91
Sample No 69	TlSe	Tl$_2$Se$_3$	1356	1167	86	1124	888	79	76
Sample No 70	ZrSi	ZrSi$_2$	1795	1401	78	1357	1289	95	92
Sample No 71	SrSn$_3$	SrSn$_5$	1609	1384	86	1311	1259	96	91
Sample No 72	Zr$_3$Sn$_2$	ZrSn$_2$	1421	1114	78	1084	1051	97	94
Sample No 73	Tl$_3$Te$_2$	TlTe	1633	1321	81	1342	1074	80	81

Table 3

Sample No.	Raw Materials mixing ratio (at.%) Si	Ni	Heating temperature (C°)	Solid phase B percentage content (wt.%)	Average Particle size (μm)	Specific surface area (m².g⁻¹)	Initial cycle *A	*B	*C	50th cycle *A	*B	*C	*D
74 a					100	0.0019	2581	2211	86	679	611	90	28
74 b					50	0.0051	2515	2295	91	651	556	95	24
74 c	92	8	1450	30	40	0.012	3005	2456	82	866	778	90	32
74 d					20	3	2958	2355	80	901	821	91	35
74 e					1	8	2922	2314	79	870	699	80	30
74 f					0.5	62	2899	2324	80	859	701	82	30
75 a					100	0.0022	2188	1977	90	2039	1937	95	98
75 b					50	0.0055	2222	1983	89	2004	1924	96	99
75 c	89	11	1400	40	40	0.01	2444	2224	91	2267	2154	95	98
75 d					20	5	2412	2195	91	2235	2123	95	98
75 e					1	10	2405	2213	92	2224	2135	96	98
75 f					0.5	45	2399	2210	92	2222	2111	95	98
76 a					100	0.0015	1711	1601	94	1635	1552	95	97
76 b					50	0.0059	1682	1572	94	1688	1621	96	97
76 c	82.5	17.5	1350	60	40	0.011	1903	1792	94	1829	1756	96	98
76 d					20	5.1	1889	1755	93	1810	1720	95	98
76 e					1	9.9	1872	1768	94	1824	1733	95	98
76 f					0.5	47	1905	1810	95	1848	1774	96	98
77 a					100	0.0025	1623	1411	87	1441	1383	96	98
77 b					50	0.0052	1611	1421	88	1451	1378	95	97
77 c	69	31	1200	95	40	0.01	1798	1594	89	1627	1562	96	98
77 d					20	4	1841	1633	89	1684	1600	95	98
77 e					1	10	1839	1629	89	1680	1596	95	98
77 f					0.5	47	1829	1615	88	1666	1583	95	98
78 a					100	0.0017	1212	915	75	944	897	95	98
78 b					50	0.0049	1129	992	87	1002	962	96	97
78 c	68	32	1200	97	40	0.012	1348	1201	89	1239	1176	95	98
78 d					20	5.7	1355	1182	87	1219	1158	95	98
78 e					1	9.8	1385	1175	85	1212	1156	95	98
78 f					0.5	47	1392	1169	84	1193	1146	96	98

*A: Charge capacity (mAh.cm⁻³)
*B: Discharge capacity (mAh.cm⁻³)
*C: Efficiency of charge & discharge (%)
*D: Discharge capacity Sustainable rate(%)

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Table 4

	Negative electrode material composition	Average particle size (µm)	Specific surface area ($m^2 \cdot g^{-1}$)	Initial cycle			50th cycle			*D
				*A	*B	*C	*A	*B	*C	
Conventional case 1a	Si	100	0.0025	4811	680	14	24	3	13	0
Conventional case 1b		50	0.0054	4798	650	14	15	2	13	0
Conventional case 1c		40	0.01	5522	811	15	11	1	9	0
Conventional case 1d		20	5	5318	823	16	14	1	7	0
Conventional case 1e		1	10.1	5415	844	16	17	4	24	0
Conventional case 1f		0.5	47	5311	850	16	14	5	36	0
Conventional case 2a	Si+C	100	0.0031	1691	475	28	88	14	16	3
Conventional case 2b		50	0.0054	1711	451	26	91	15	17	3
Conventional case 2c		40	0.011	2255	601	27	110	21	19	3
Conventional case 2d		20	7	2169	559	26	115	25	22	4
Conventional case 2e		1	10	2214	584	26	121	38	31	7
Conventional case 2f		0.5	49	2267	599	26	109	34	31	6
Conventional case 3a	C (Natural Graphite)	100	0.0021	491	447	91	445	443	100	99
Conventional case 3b		50	0.0052	484	451	93	447	446	100	99
Conventional case 3c		40	0.001	490	440	90	438	436	100	99
Conventional case 3d		20	4	488	448	92	445	444	100	99
Conventional case 3e		1	10	491	450	92	447	446	100	99
Conventional case 3f		0.5	51	490	449	92	446	445	100	99
Conventional case 4a	Mg_2Si	100	0.0029	1159	465	40	452	451	100	97
Conventional case 4b		50	0.0054	1139	459	40	447	445	100	97
Conventional case 4c		40	0.011	1140	461	40	448	447	100	97
Conventional case 4d		20	9	1121	470	42	463	461	100	98
Conventional case 4e		1	10	1149	455	40	444	441	100	97
Conventional case 4f		0.5	49	1155	459	40	451	450	100	98

*A: Capacity charge ($mAh \cdot cm^{-3}$)
*B: Discharge capacity ($mAh \cdot cm^{-3}$)
*C: Efficiency of charge and discharge (%)
*D: Discharge capacity sustainable rate (%)

Table 5

Sample No.	Discharge capacity change rate (%)				
	Si exposed area ratio (%)	0.7mA.cm^{-2}	1.4mA.cm^{-2}	2.0mA.cm^{-2}	3.0mA.cm^{-2}
79a	0	80	73	51	44
79b	2	100	93	87	75
79c	5	100	95	91	86
79d	10	100	96	92	88
79e	20	100	96	93	89
79f	40	100	96	95	90
79g	60	100	97	94	89
79h	80	100	96	95	90
79i	100	100	97	95	91

Table 6

Positive electrode material	Negative electrode paste composition (weight %)			Discharge capacity sustainable rate (%)
	Negative electrode material	PVDF	Natural Graphite	
LiCoO$_2$	92	5	3	63
	90	5	5	80
	65	5	30	85
	45	5	50	83
	15	5	80	80
	10	5	85	75
LiNiO$_2$	92	5	3	62
	90	5	5	81
	65	5	30	84
	45	5	50	83
	15	5	80	82
	10	5	85	70
LiMn$_2$O$_4$	92	5	3	62
	90	5	5	81
	65	5	30	84
	45	5	50	83
	15	5	80	82
	10	5	85	70

Claims

1. A negative electrode material for non-aqueous electrolyte secondary battery comprising:

   a composite particle comprising;

   a core formed by a solid phase A, and
   a solid phase B wrapping one of partial core and entire core,
   wherein said solid phase A comprising one of the following material:

   lithium,
   at least one element being able to alloy with lithium,
   solid solution including said element being able to alloy with lithium, and
   an intermetallic compound including said element being able to alloy with lithium,
   wherein said solid phase B having a different component from the solid phase A and comprising one of the following material:

   solid solution including said element being able to alloy with lithium, and
   an intermetallic compound including said element being able to alloy with lithium,

2. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein said composite particle is solidified and deposited by peritectic phenomenon.

3. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein said solid phase B is a mixed conductor having electronic conductivity and lithium ionic conductivity.

4. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein said solid phase A comprises one of the following materials:

   lithium,
   at least one of the elements being able to alloy with lithium including, zinc, cadmium, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, antimony and bismuth,
   solid solution including said element being able to alloy with lithium,
   an intermetallic compound including said element being able to alloy with lithium.

5. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein said solid phase B comprises one of the following materials:

   solid solution including at least one element selected from alkaline earth element and transition metal element, and
   an intermetallic element including at least one element selected from alkaline earth element and transition metal element.

6. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein said solid phase A comprises silicon, and said solid phase B comprises nickel silicides.

7. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 1, wherein a percentage content of the solid phase B in said composite particle ranges between 40 and 95 weight %.

8. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 6 or Claim 7, wherein said composite particle has the following dimensions:

   average particle size: 1-40 μm
   specific surface area: 0.01-10 $m^2 \cdot g^{-1}$

9. The negative electrode material for non-aqueous electrolyte secondary battery as defined in Claim 6, wherein said solid phase A exposes on the particle surface 5-40% of an overall surface area of the particle.

10. A non-aqueous electrolyte secondary battery having a negative electrode using the material as defined one of the claims 1 through 9.

11. A non-aqueous electrolyte secondary battery having a negative electrode using the material as defined one of the claims 1 through 9, wherein carbon powder is added to said material of the negative electrode within a range of 5 to 80 weight %.
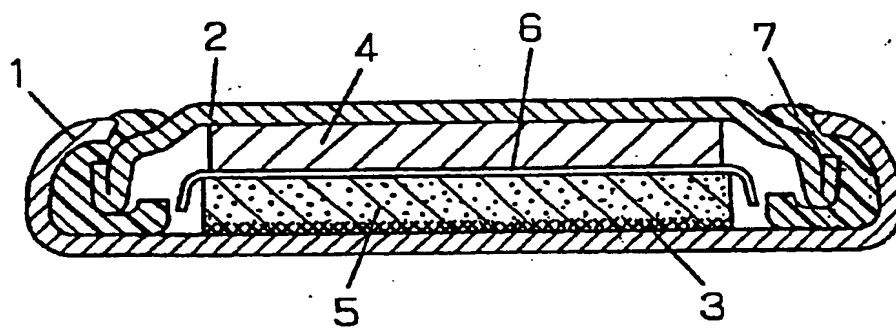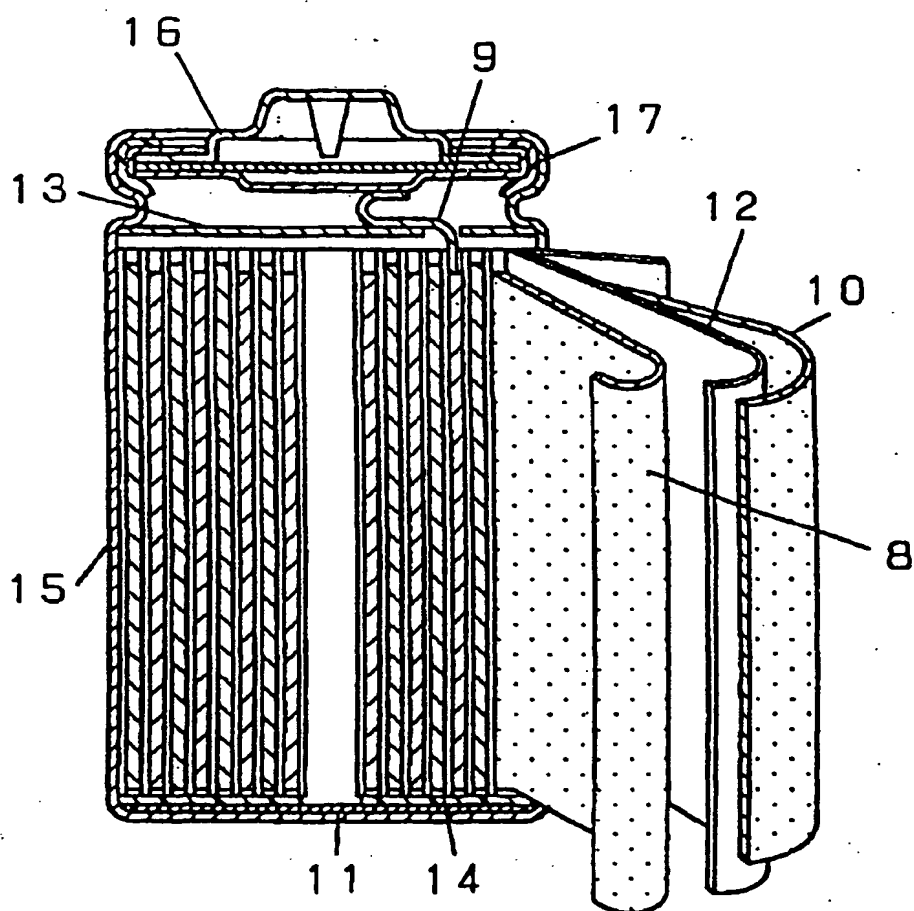
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Fig. 1

Fig.2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 98 11 0110

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 4 632 889 A (MCMANIS GEORGE E ET AL) 30 December 1986 * claims 1-6 *	1-11	H01M4/40 H01M4/36 H01M4/02
A	EP 0 693 568 A (HOPE TECHN INC) 24 January 1996 * claims 1-6 *	1-11	
A	US 4 950 566 A (HUGGINS ROBERT A ET AL) 21 August 1990 * claims 1-4 *	1-11	
A	US 4 495 258 A (LE MEHAUTE ALAIN ET AL) 22 January 1985 * claims 1-14 *	1-11	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 September 1998	Battistig, M

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